

Electrocatalytic dechlorination of polychloroethylenes at silver cathode

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Abstract In this study, silver was considered as a catalytic electrodic material for the reduction of polychloroethylenes for possible application in environmental remediation and/or as an auxiliary process in the industrial chlorination of ethylene for production of vinyl chloride monomer. The electroreduction of tetrachloroethylene (PCE) and trichloroethylene (TCE), which are the most hazardous chlorinated ethylenes, was investigated at a Ag electrode in DMF under conditions of controlled proton availability. For the sake of comparison also 1,1-dichloroethylene (1,1-DCE) and 1,2-dichloroethylene were considered. Voltammetric investigations point out that Ag possesses good catalytic activities for the reduction of PCE, TCE, and 1,1-DCE as attested by the remarkable positive shifts (up to 0.46 V) of the reduction potentials with respect to GC, considered to be a non-catalytic material. In contrast, Ag shows no appreciable catalytic effect for 1,1-DCE. Apart from the case of 1,1-DCE, the presence of acetic acid (HAc) exalts the catalytic activity of silver, increasing the anodic shifts of the reduction potentials to about 0.57–0.70 V with respect to GC. Controlled-potential electrolyses have shown that both PCE and TCE are mainly reduced to acetylene and ethylene with overall yields exceeding 95 % after 100 % conversion. The distribution between these two products as well as formation of intermediates, which however remained always quite low, was found to be affected by the presence of proton

donors such as H₂O and HAc. A common reduction mechanism observed for both PCE and TCE involves the α,β -elimination of two Cl[−] ions triggered by the electron transfer. This leads to the formation of dichloroacetylene or chloroacetylene, which are further reduced at the electrode according to a sequential hydrodehalogenation leading to acetylene. The latter can be further reduced to ethylene.

Keywords Polychloroethylenes · Silver cathode · Electrocatalysis · Pollutant conversion · Ethylene recycling

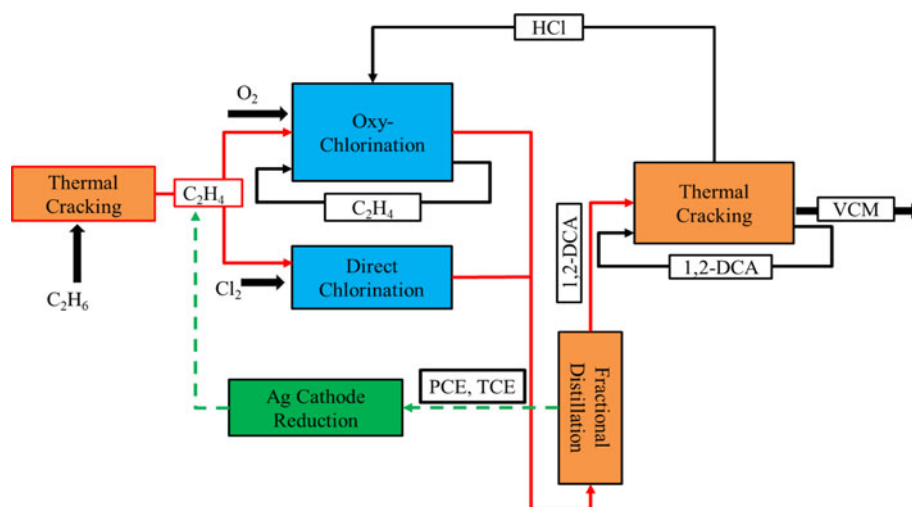
1 Introduction

Polyvinyl chloride is one of the most commonly used thermoplastic materials in the world with a demand that exceeds 35 million tonnes per year and it is rated second only after polyethylene [1]. This establishes vinyl chloride monomer (VCM) as one of the largest commodity chemicals produced in both the United States and Europe. Nowadays, VCM is produced commercially by pyrolytic decomposition of 1,2-dichloroethane (1,2-DCA), which may be produced by the direct chlorination of ethylene or by oxychlorination of the olefin in the presence of oxygen and hydrogen chloride (Fig. 1). Pyrolysis of 1,2-DCA produces vinyl chloride together with an equal amount of hydrogen chloride as a co-product, which is recycled to the oxychlorination reactor where it is completely consumed [2]. Besides 1,2-DCA, both processes yield a mixture of products, which are separated by fractional distillation into a light fraction (very volatile compounds), 1,2-DCA (main product) and a heavy fraction containing trichloroethylene (TCE) and tetrachloroethylene (PCE). The last two polychloroethylenes (PyCEs) are classified as hazardous compounds and are expensive to treat and dispose of. Thence,

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Fig. 1 Conventional balanced process for VCM production. Dashed line represents a possible implementation of the whole process



in the perspective of reducing the economic and environmental impact of the by-products, a viable strategy is required to convert TCE and PCE to non-hazardous products if not to more valuable products to be reutilized in the same VCM production cycle (Fig. 1, dashed pathway).

Because of the highly electronegative character of the chlorine atom, halogenated organic compounds are in general susceptible to reduction, which involves removal of a halogen atom(s) from the molecule. In the last decades several reduction methods, including zero-valent metal particles [3, 4], microbial cultures [5] and catalytic electroreduction [6], have attracted much research attention, which has shown that reductive dehalogenation is a valid strategy for the treatment of polychlorohydrocarbons. In particular, the electrochemical route presents advantages over other techniques since it requires intrinsically milder experimental conditions and allows enhanced reduction kinetics, reduced treatment time and higher selectivity [7]. The electrochemical reductive dechlorination of alkyl halides follows essentially two reaction routes: hydrodechlorination involving the replacement of a chlorine atom with a hydrogen one [8] and α,β -dechlorination which involves the removal of two Cl atoms from adjacent carbon atoms which thus form an additional C–C bond [9]. The preferred reaction route depends on the molecular structure of the target molecule (geminal or vicinal alkyl halide) as well as on the acid–base properties of the reaction environment.

A major issue of crucial importance in the perspective of making electrochemical methodologies attractive from the applicative point of view is the development of electrodic materials with high catalytic activities. In fact, the electrochemical reduction of C–Cl bonds involves very high overpotentials because reductive cleavage involves both electron transfer (ET) and bond breaking. Among the electrodes investigated Ag has shown to be one of the most

promising materials for the electroreduction of polychloroalkanes, possessing excellent catalytic properties both in terms of current efficiency and selectivity [9–12].

The research reported here was aimed to understand whether Ag cathode possesses catalytic activities toward the reduction of PyCEs and how the molecular structure of PyCE can affect the dechlorination mechanism and/or the catalytic activity of Ag. To this end, we have focused on the electrochemical reduction of PCE and TCE dissolved in an organic solvent. In fact, since PyCEs are highly soluble in organic solvents, highly concentrated solutions can be prepared and electrolyzed with high current densities. Therefore, we wish to verify whether Ag has the long-term stability required for its successful employment in preparative scale electrolysis. The upshots of this research may have interesting implications for the development of an auxiliary process for the conversion of PyCEs, produced in the VCM process, to ethylene (Fig. 1, dashed pathway). Indeed, it has been recently reported that 1,1,1,2-tetrachloroethane can be electrocatalytically reduced at Ag or Cu to give ethylene as the principal product [9, 13]. In addition, the electrochemical dechlorination can be achieved in bulk PCE or TCE after addition of an appropriate supporting electrolyte or in micro-fluidic systems which avoid the inconvenient employment of a supporting electrolyte [14]. This means that great amounts of PCE may be converted to less dangerous or even more valuable products in a short period of time.

2 Experimental

2.1 Chemicals

DMF (WWR, 99 %) was treated with anhydrous Na_2CO_3 and doubly distilled at reduced pressure under a N_2

atmosphere. Tetraethylammonium perchlorate (Et_4NClO_4), tetraethylammonium chloride (Aldrich, 98 %), and tetrapropylammonium tetrafluoroborate (Pr_4NBF_4) (Fluka, >98 %) were recrystallized from ethanol–water (2:1), dichloromethane–acetone–hexane (2:2:1) and ethanol, respectively, and were dried in a vacuum oven at 60 °C (Et_4NClO_4) or 70 °C. 1,1,2,2-tetrachloroethylene, 1,1,2-trichloroethylene, 1,2-dichloroethylene (1,2-DCE), and 1,1-dichloroethylene (1,1-DCE) were high purity reagents purchased from Sigma-Aldrich and were used without further purification.

2.2 Electrochemical instrumentation

Electrochemical measurements were performed on a computer-controlled EG&G PARC Model 273A potentiostat equipped with a digital coulometer. Cyclic voltammetry experiments were carried out in a three electrode cell system with a glassy carbon (GC) disk or a Ag disk as working electrode. The counter electrode and the reference electrode were a Pt wire and $\text{Ag}|\text{AgCl}|\text{Me}_4\text{NCl}(\text{sat})$ in CH_3CN -DMF (3:1), respectively. The latter was calibrated after each experiment against the ferrocenium/ferrocene couple. The potentials measured against the $\text{Ag}|\text{AgCl}|\text{Cl}^-$ reference electrode were converted to the SCE scale, to which all potentials in the paper are referred, by using $E_{\text{Fc}^+/\text{Fc}}^0 = 0.475 \text{ V}$ versus SCE in DMF. The working electrodes were built from a 3 mm diameter GC rod (Tokai, GC-20) or from a 2 mm diameter Ag wire (Alfa Aesar, 99.999 %) and were cleaned and activated before each experiment as previously described [6]. Controlled-potential electrolyses were carried out in a divided cell using a Ag cylinder of 10 cm² area, a Pt foil as counter electrode and $\text{Ag}|\text{AgCl}|\text{Cl}^-$ as a reference electrode. All experiments were carried out at 25 °C.

2.3 Analytical methods

Electrolysis products in the liquid phase were analyzed as headspace samples after pre-concentration by means of solid-phase microextraction (SPME). The analyses were performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector and a DB-5 ms 30 m \times 0.25 mm \times 0.25 μm capillary column (Agilent Technologies, USA). The SPME apparatus and fibers, silica fibers coated with a 75 μm Carboxen polydimethylsiloxane, were purchased from Supelco. Authentic compounds were used for the identification and quantification of the products. A single standard mixture, 10^{-2} M in PCE, TCE, 1,1-DCE, and 1,2-DCE was prepared in DMF containing 0.1 M Pr_4NBF_4 and was used as a primary stock solution; standard solutions at different concentrations of PyCEs were prepared by appropriate dilution of this stock solution. All quantitative

determinations were based on calibration curves. Details on procedures of sample preparation and GC analysis have been previously published [8].

The electrolysis products in the gas phase were analyzed on a HP 6890 system GC equipped with a flame ionization detector and a HP Plot Q 30 m \times 0.537 mm \times 0.40 μm capillary column (Agilent Technologies, USA). A sample was withdrawn from the reaction cell with a gas syringe through a septum cap and injected directly into the GC. Identification of the products and construction of calibration curves for their quantitative determination were based on a certified gas mixture acquired on purpose.

The concentration of Cl^- produced during electrolyses was electrochemically determined by cyclic voltammetry employing a polycrystalline silver electrode. An Ag layer on a Pt sphere (diameter = 1.5 mm) was prepared by electrodeposition of Ag from a 0.1 M $\text{KAg}(\text{CN})_2$ bath at a constant current density of 0.4 mA/cm² for 6 h. Before electrodeposition the Pt sphere was pickled in 0.1 M HNO_3 at a constant current density of 4 mA/cm² for 30 min. In DMF + 0.1 M Pr_4NBF_4 , voltammetry of Cl^- at Ag shows two oxidation peaks with peak currents that are proportional to the concentration of the ion (see Supporting Information). Anhydrous Et_4NCl was used to construct calibration curves (from 0 to 50 mM) for Cl^- determination in DMF + 0.1 M Pr_4NBF_4 .

3 Results and discussion

3.1 Cyclic voltammetry

Cyclic voltammograms of $\text{Cl}_2\text{C}=\text{CCl}_2$ (PCE), $\text{Cl}_2\text{C}=\text{CHCl}$ (TCE), $\text{Cl}_2\text{C}=\text{CH}_2$ (1,1-DCE), and $\text{ClCH}=\text{CHCl}$ (1,2-DCE) at GC and Ag in DMF + 0.1 M Et_4NBF_4 are shown in Fig. 2, whereas the peak potentials measured at $\nu = 0.2 \text{ V/s}$ both in the absence and presence of acetic acid (HAc) are summarized in Table 1. Reduction of PCE at GC gives rise to a single irreversible peak at -2.09 V (Fig 2a); the absence of any other following peaks at more negative potentials ruled out the formation of less chlorinated ethylenes as reduction intermediates. TCE shows three reduction peaks; the first peak at -2.28 V is followed by a rather small peak at -2.54 V and a third one appearing only as a shoulder of the solvent discharge current (Fig 2b). The first peak obviously refers to the reduction of the reagent, whereas, based on peak location, the second and third peaks can be assigned to the reduction of 1,1-DCE (Fig 2c). Finally, 1,2-DCE exhibits a single irreversible reduction peak at -2.63 V (Fig. 2d).

The solid lines in Fig. 2 illustrate the voltammetric patterns of PyCEs at Ag in DMF + 0.1 M Et_4NBF_4 . PCE and TCE give sharp reduction peaks at -1.86 and -1.82 V ,

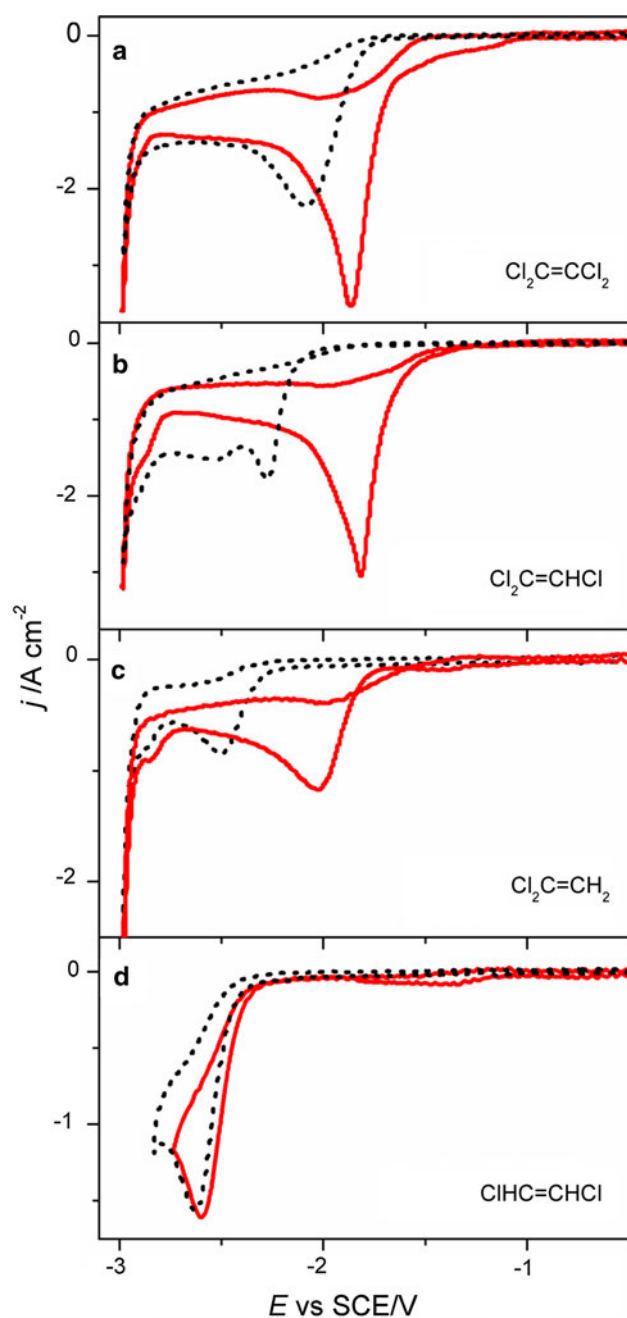


Fig. 2 Cyclic voltammetry of 2 mM (a) $\text{CCl}_2=\text{CCl}_2$, (b) $\text{CCl}_2=\text{CHCl}$, (c) $\text{CCl}_2=\text{CH}_2$ and (d) $\text{CHCl}=\text{CHCl}$ recorded at $\nu = 0.2 \text{ Vs}^{-1}$ in DMF + 0.1 M Et_4NClO_4 at GC (dashed line) and Ag (solid line)

respectively (Fig. 2a, b), indicating that the electrode process involves adsorption phenomena, which may account for the catalytic activity of Ag. In fact, a comparison between the voltammetric responses of all PyCEs at Ag and GC electrodes shows that all peaks are positively shifted at Ag with respect to GC. This positive shift accounts for the catalytic effect, which can be expressed as the difference between the peak potentials at Ag and GC, that is $\Delta E_p = E_p^{\text{Ag}} - E_p^{\text{GC}}$. As

Table 1 Voltammetric data for polychloroethylenes (2 mM) in DMF + 0.1 M Et_4NClO_4 in the absence and presence of acetic acid (HAc)

Substrate	GC E_p^a (V)	E_p^b (V)	Ag E_p^a (V)	E_p^b (V)	$\Delta E_p^{\text{cat}, c}$ (V)	$\Delta E_p^{\text{cat}, c}$ b, c (V)
PCE	-2.094	-2.063	-1.858	-1.383	0.236	0.680
TCE	-2.276	-2.228	-1.816	-1.662	0.460	0.566
1,1-DCE	-2.503	-2.409	-2.047	-1.705	0.456	0.704
1,2-DCE	-2.631	-2.663	-2.601	-2.607	0.030	0.056

^a E_p (vs SCE) measured at $\nu = 0.2 \text{ Vs}^{-1}$

^b In the presence of HAc

^c $\Delta E_p^{\text{cat}} = E_p^{\text{Ag}} - E_p^{\text{GC}}$

shown by the values of ΔE_p reported in Table 1, Ag possesses good catalytic activities for PyCEs except in the case of 1,1-DCE. Interestingly, the electrocatalytic activity of Ag is further enhanced by the presence of HAc, which shifts the reduction peaks to even more positive potentials without sensibly affecting the peak current or the reduction behavior (Table 1, last column). In the presence of HAc, the catalytic effect varies with molecular structure in the order $\text{ClCH}=\text{CHCl} \ll \text{CCl}_2=\text{CHCl} < \text{CCl}_2=\text{CCl}_2 < \text{CCl}_2=\text{CH}_2$, which underscores the importance not only of the number of chlorine atoms but also their distribution in the molecule.

The mechanism of the dissociative electron transfer (DET) to PyCEs has been previously investigated [15]. Reductive cleavage of the C–Cl bond may basically follow two mechanisms: a concerted mechanism in which ET and bond rupture occur in a single step (Eq. 1) or a stepwise mechanism involving the intermediate formation of a labile radical anion $\text{RCl}^{\bullet-}$ (Eqs. 2, 3). Whichever the mechanism, DET to RCl produces a radical R^{\bullet} , which is easier to reduce than the starting molecule (Eq. 4).

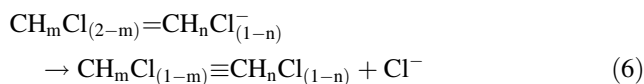
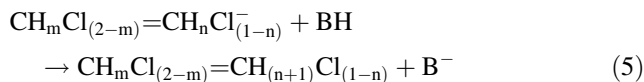
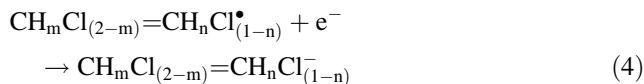
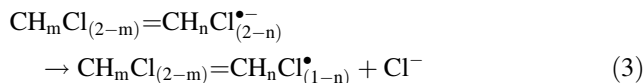
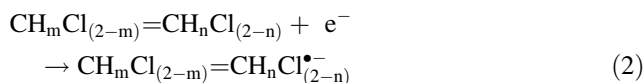
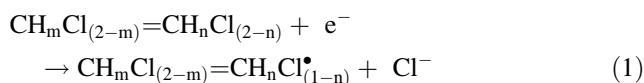


Table 2 Electrolyses of PCE (10 mM) and TCE (10 mM) in 20 mL of DMF + 0.1 M Pr₄NBF₄ at a Ag cathode

Entry	Substrate	E_{app} (V vs SCE)	n^a	CCl ₂ CCl ₂ (%)	CCl ₂ CHCl (%)	CHClCHCl (%)	CClCCl (%)	CHCCl (%)	CH ₂ CH ₂ (%)	CHCH (%)	CE ^b (%)
1	PCE	−2.05	4.8	0	–	–	–	–	–	43.7	55
2a	PCE + HAc ^c	−1.35	6.00	20.6	4.3	–	–	–	21.7	54.9	85
2b		−1.95	10.00	0	0	–	–	–	65.3	29.5	70
3b	TCE	−1.90	4.00	–	0	–	–	–	–	79.9	80
4a	TCE + H ₂ O ^d	−1.70	2.00	–	18.6	0.8	22.2	1.0	<0.1	49.6	101
4b		−2.20	3.43	–	0	0	0	0	<0.1	85.9	100
5a	TCE + HAc ^c	−1.70	5.26	–	2.4	2.4	–	–	23.5	74.7	85
5b		−2.20	6.60	–	0	<0.1	–	–	31.7	66.1	69

Values in percentage were calculated with respect to the starting substrate

^a Number of electrons transferred per molecule of initial substrate

^b CE = current efficiency = (theoretical charge for product formation)/(experimental charge consumption)

^c In the presence of 0.1 M CH₃CO₂H

^d In the presence of 2 M H₂O

The competition between stepwise and concerted mechanisms depends on whether the incoming electron can be accommodated in a low lying π^* orbital or it has to occupy a σ^* orbital, in which case concomitant bond breaking becomes thermodynamically more favored than $\text{RCl}^{\bullet-}$ formation. Costentin et al. [15] have reported that the first stage of the electrochemical reduction of PyCEs at GC in DMF involves the intermediacy of the π^* anion radical (stepwise mechanism). In the case of Ag, the evaluation of the DET mechanism is not straightforward since catalytic effects are present. In fact, adsorption of the reagent and/or its reduction intermediates and products (RX , $\text{RX}^{\bullet-}$, R^{\bullet} , and X^-) at the Ag surface can significantly affect both the kinetics and thermodynamics of the process [16–18]. However, regardless of whether the process follows a stepwise or a concerted mechanism, it leads to the generation of a vinyl radical that can be further reduced to a vinyl carbanion in an overall two electron process. The electrogenerated vinyl carbanion may either undergo protonation thus leading to hydrodechlorination of the carbon-chlorine bond (Eq. 5) or expel a chloride ion to yield the corresponding alkyne (Eq. 6). The proton donor BH might be the residual water in the solvent, the background electrolyte, PyCE itself or any added acid. Voltammetric analysis cannot discern which of the two pathways is more favored since the voltammograms of TCE and PCE do not provide full information concerning the reaction products.

3.2 Electrolysis of tetrachloroethylene

For the electrolysis, Pr₄NBF₄ was preferred to Et₄NBF₄ because, in the presence of a strong base such as electrogenerated carbanions, tetra-alkyl ammonium cations R_4N^+ often undergo Hoffman degradation to an alkene $\text{R}(-\text{H})$

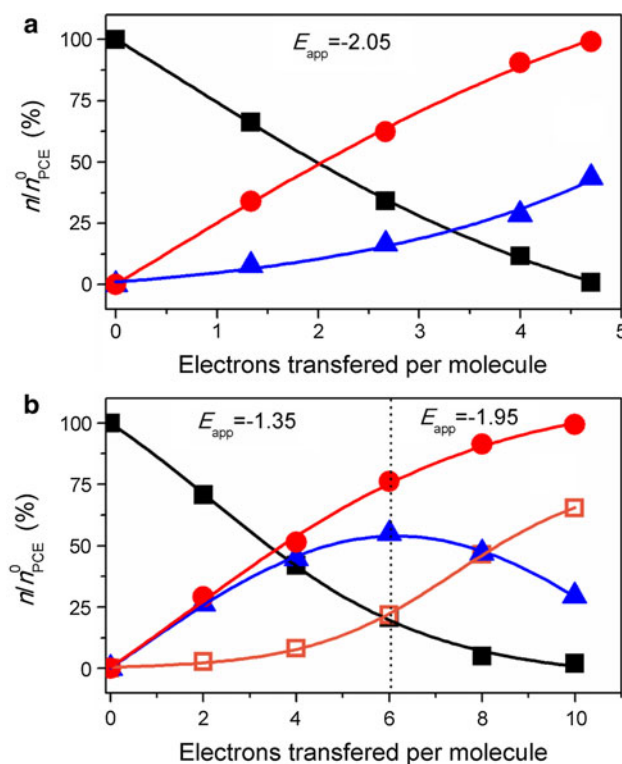
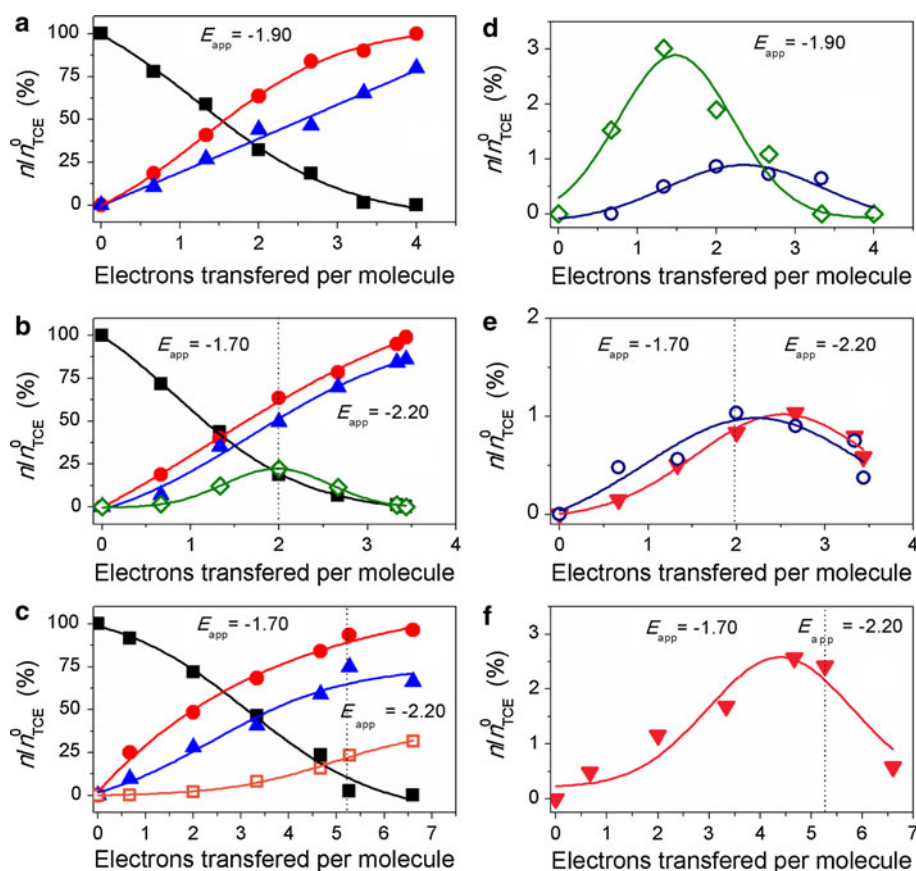


Fig. 3 Electrolyses of 10 mM $\text{CCl}_2=\text{CCl}_2$ at Ag in DMF + 0.1 M Pr₄NBF₄ performed in the absence of any added proton donor (a) or in the presence of 0.1 M CH₃CO₂H, (b). Concentration profiles: (closed square) $\text{Cl}_2\text{C}=\text{CCl}_2$; (closed circle) Cl^- ; (triangle) $\text{CH}\equiv\text{CH}$; (open square) $\text{CH}_2=\text{CH}_2$. The inserted numbers indicate E_{app} , whereas the vertical line indicates a change of E_{app}

and R_3N . Thus, the presence of Et₄NBF₄ might produce ethylene, which is one of the possible products of $\text{Cl}_2\text{C}=\text{CCl}_2$ reduction. This possibility is obviously avoided in the case Pr₄NBF₄ is employed as supporting

Fig. 4 Electrolyses of 10 mM $\text{Cl}_2\text{C}=\text{CHCl}$ at Ag in DMF + 0.1 M Pr_4NBF_4 performed in the absence of any added proton donor (**a, d**) or in the presence either of H_2O 2 M (**b, e**) or 0.1 M $\text{CH}_3\text{CO}_2\text{H}$, (**c, f**). Concentration profiles: (closed square) $\text{Cl}_2\text{C}=\text{CHCl}$; (closed circle) Cl^- ; (triangle) $\text{CH}\equiv\text{CH}$; (diamond) $\text{ClC}\equiv\text{CCl}$; (open square) $\text{CH}_2=\text{CH}_2$; (open circle) $\text{ClC}\equiv\text{CH}$; (inverted triangle) $\text{ClCH}=\text{CHCl}$. The inserted numbers indicate E_{app} , whereas the vertical lines indicate when it was changed



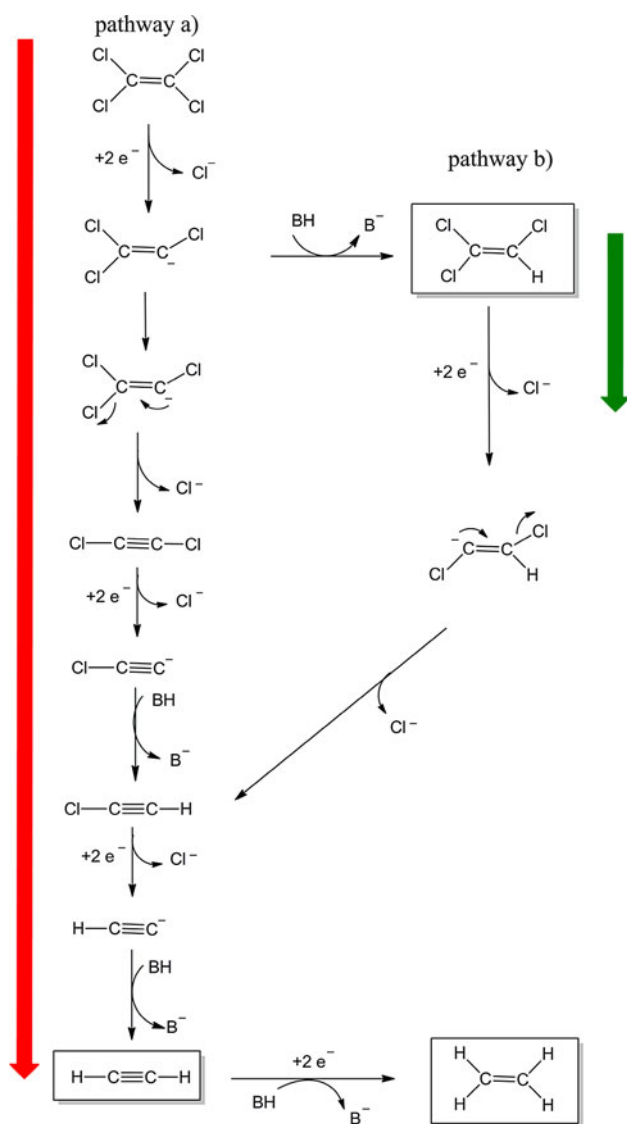
electrolyte. Electrolyses of $\text{Cl}_2\text{C}=\text{CCl}_2$ were carried out potentiostatically at Ag in DMF + 0.1 M Pr_4NBF_4 at -2.05 V, i.e., just after its single reduction peak. The results of the experiments performed both in the absence and presence of 0.1 M HAc, are summarized in Table 2 (entries 1 and 2), whereas Fig. 3 shows the concentration profiles of the starting substrate and its principal reduction products observed during electrolysis. When no acid was added, complete conversion of $\text{Cl}_2\text{C}=\text{CCl}_2$ yielded only 43.7 % of acetylene; no other products or intermediates were observed (Table 2, entry 1 and Fig. 3a). Although the carbon mass balance is quite low, complete dehalogenation of $\text{Cl}_2\text{C}=\text{CCl}_2$ was achieved as testified by the production of Cl^- , which reached ca. 100 % at the end of electrolysis. Note that since each $\text{Cl}_2\text{C}=\text{CCl}_2$ molecule produces 4Cl^- , the concentration of the ion was normalized by a factor of 4 so that in Fig. 3 the reported yield n/n_{PCE}^0 will vary from 0 to 100 %. These results suggest that reaction pathways other than hydrodechlorination or α,β -elimination are also present. Although the nature of these reactions is not known, it is clear that they consume less charge than required for the complete dechlorination to ethylene. Dichloroacetylene and chloroacetylene were not detected. However, it is possible that at the applied potential they can

be concomitantly reduced with the starting reagent at the Ag cathode.

Figure 3b shows variations of the principal reduction products of $\text{Cl}_2\text{C}=\text{CCl}_2$ observed during preparative electrolyses in the presence of 0.1 M HAc. In the first step at -1.35 V, after the consumption of the theoretical $6e^-$ per molecule of PCE, 79.4 % of the starting reagent was converted resulting in the formation of acetylene (54.9 %), ethylene (21.7 %), and TCE (4.3 %) (Table 2, entry 2a). In the second step, the applied potential was shifted to -1.95 V; after an overall consumption of $10e^-$ per molecule, both PCE and TCE completely disappeared, while the yield of ethylene increased to 65.3 % with the concomitant decrease of acetylene yield to 29.5 %. Also in this case the Cl^- mass balance indicates that all chlorinated intermediates were exhaustively dechlorinated.

3.3 Electrolysis of trichloroethylene

The concentration profiles observed during electrolyses of TCE at Ag in DMF + 0.1 M Pr_4NBF_4 , performed in the absence or presence of an added proton source, are shown in Fig. 4. As in the case of Fig. 3, the yield of Cl^- was normalized by the number of Cl atoms (i.e., 3) present in



Scheme 1 Reaction scheme for the reduction of tetrachloroethylene

each molecule of TCE. The yields of the products are reported in Table 2 (entries 3–5). The distribution of both the final products and reduction intermediates is significantly affected by the proton availability of the reaction medium. When no proton donor was added, 79.9 % acetylene was obtained after total conversion of TCE which consumed $4e^-$ per molecule of substrate (Table 2, entry 3). It is worth noting that the formation of acetylene increases throughout the electrolyses (Fig. 4a), which clearly indicates that besides the reagent all the intermediates are reducible at Ag at the imposed potential of -1.90 V. During electrolysis, small amounts of dichloroacetylene and chloroacetylene were detected as intermediates; the concentrations of both intermediates follow bell-shaped trends reaching maximum values of 3 % ($\text{ClC}\equiv\text{CCl}$) and 1 % ($\text{ClC}\equiv\text{CH}$) (Fig. 4d).

The electrolysis of TCE, carried out at $E_{\text{app}} = -1.70$ V in the presence of 2 M H_2O , converted 81.4 % of the starting substrate after a charge consumption of $2e^-$ per molecule of TCE and yielded 49.6 % of acetylene together with dichloroacetylene (22 %), 1,2-DCE (0.8 %) and chloroacetylene (1 %) (Table 2, entry 4a). Further electrolysis at -2.20 V resulted in a complete dechlorination of TCE and its intermediates, and yielded 85.9 % of acetylene (Table 2, entry 4b). The detection of 1,2-DCE indicates that H_2O protonates the electrogenerated vinyl carbanion. The presence of H_2O also promotes dehydrodechlorination of TCE to dichloroacetylene.

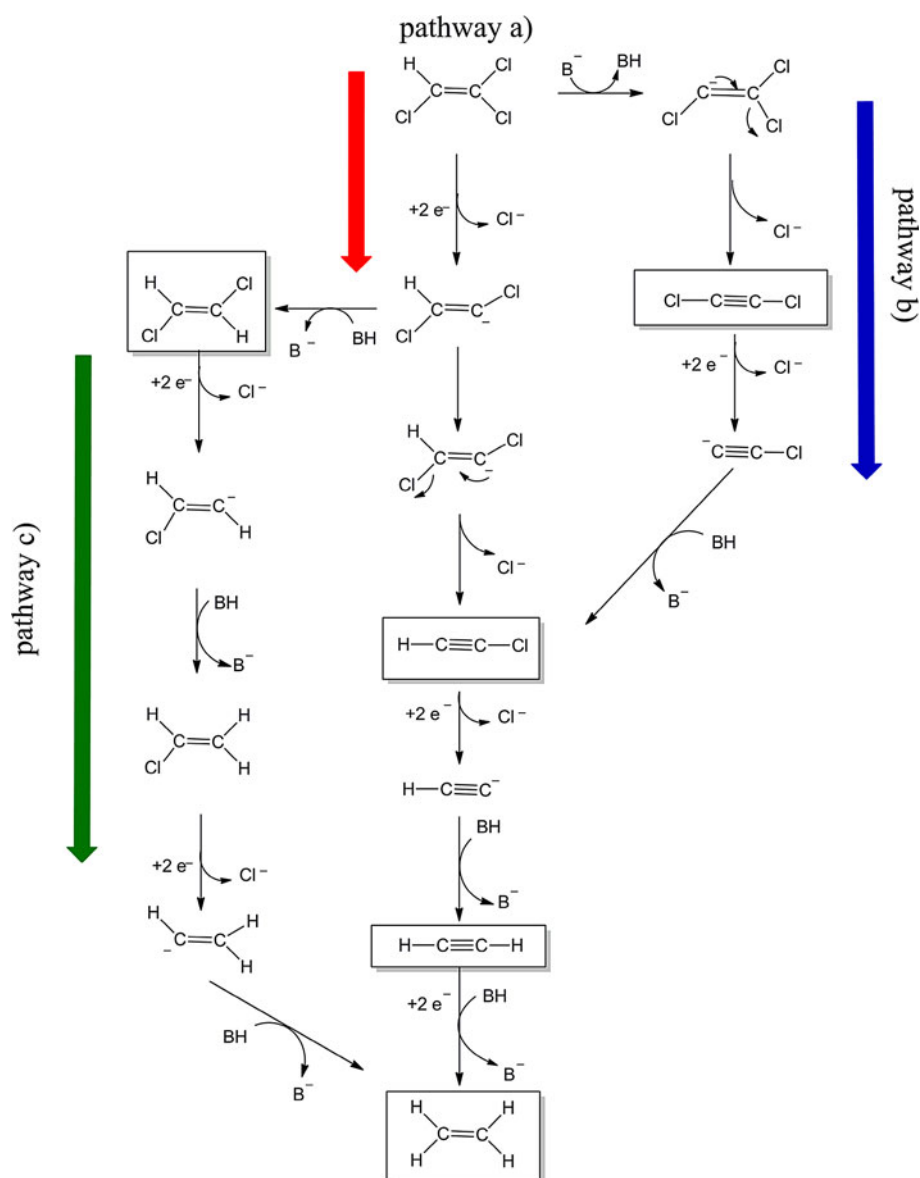
Figure 4c,f shows the trends of the main reduction products observed during the electrolysis of TCE in the presence of 0.1 M HAc. In comparison with the electrolysis performed in the presence of H_2O , the yield of acetylene reaches a maximum value of 75 % but then decreases to 66 % in the last step, while ethylene concentration increases throughout the experiment reaching a maximum yield of 32 % (Table 2, entry 5). Neither chloroacetylene nor dichloroacetylene was detected. On the contrary, 1,2-DCE (2.4 %) was found as an intermediate.

In all cases, complete dechlorination of TCE as well as its chlorinated reduction intermediates was achieved as testified by quantitative production of Cl^- . It is interesting to note that complete dechlorination of both PyCEs at Ag is accomplished with moderate to high current efficiencies (Table 2, last column).

3.4 Reduction mechanism of PCE and TCE

According to the results reported herein and considering that chlorinated ethylenes were not detected during electrolysis of PCE, reduction of $\text{Cl}_2\text{C}=\text{CCl}_2$ in DMF + 0.1 M Pr_4NBF_4 undergoes an α,β -elimination mechanism triggered by electron transfer (scheme 1, pathway a). The first reduction step leads to the formation of a vinyl carbanion, which rapidly loses Cl^- to give dichloroacetylene. The successive steps are a series of reduction steps each involving two electron transfers, removal of a chloride ion and protonation until acetylene is formed. In the presence of a good proton source, the vinyl carbanion generated in the first step can in principle be protonated to TCE according to a hydrodechlorination mechanism (scheme 1, pathway b). However, the low concentration of TCE detected points out that expulsion of Cl^- from $\text{Cl}_2\text{C}=\text{CCl}^-$ is much faster than protonation of the carbanion even in the presence of a good proton donor such as HAc. Indeed, only a small amount of TCE (4.3 %) was found as an intermediate. Since other chlorinated ethylenes were not detected, the occurrence of a hydrodechlorination sequence leading to ethylene is highly improbable. Therefore, a step in which acetylene is reduced

Scheme 2 Reaction scheme for the reduction of trichloroethylene



to ethylene must be considered. We have recently shown that acetylene can be reduced to ethylene at a Ag cathode [9]. This is a $2e^-$ process favored by the presence of a proton source and occurring in a sequence of electron transfer and proton transfer reactions, typical of the electrochemical reduction of unsaturated organic compounds.

In the case of TCE, a more complicated reaction mechanism is reported in scheme 2. Although there are some variations of minor importance, depending on proton availability in the medium, it is clear that chloroacetylene is a key intermediate in the electroreduction of TCE at Ag. The first step of the process leads to the formation of $\text{ClHC}=\text{CCl}^-$, which can either give chloroacetylene by β -elimination of Cl^- (scheme 2, pathway a) or undergo protonation to give 1,2-DCE (scheme 2, pathway c). Since, however, 1,2-DCE was detected in a low yield, we must

conclude that Cl^- loss is faster than protonation also for $\text{ClHC}=\text{CCl}^-$, even in the presence of HAc. In addition, since neither pathway a nor pathway c predicts formation of dichloroacetylene, which was found as an intermediate (Table 2, entry 4a), a third reaction route should be considered for its production. We propose that a base B^- , electrogenerated either directly or indirectly, deprotonates the starting reagent generating a vinyl carbanion $\text{Cl}_2\text{C}=\text{CCl}^-$ that can expel Cl^- to yield $\text{ClC}\equiv\text{CCl}$ (Scheme 2, pathway b). The nature of the base B^- is not known; it may be an electrogenerated carbanion or OH^- arising from protonation of carbanions by H_2O . The effect of H_2O addition on the yield of dichloroacetylene (Table 2, entry 4) lends some credit to the hypothesis of OH^- involvement. In fact, the presence of H_2O favors both pathway b and pathway c, increasing the yields of both

dichloroacetylene and 1,2-DCE. It is thence evident that H_2O plays a double role in the electrolysis of TCE at Ag: it favors the hydrodehalogenation mechanism by the protonation of electrogenerated vinyl carbanions on one hand, while it generates OH^- which promotes the dehydrodechlorination mechanism on the other hand. The presence of a good proton donor such as HAc hampers *pathway b* simply because the acetate ion cannot deprotonate TCE.

According to the *pathway c* of Scheme 2, TCE can be reduced to 1,2-DCE and then to VCM, which can be finally reduced to ethylene. However, the small amount of 1,2-DCE (<3 %) detected suggests that ethylene, which was obtained with a yield as high as 31.7 %, does not arise from reduction of this intermediate. Therefore, the only way to explain the formation of ethylene is by reduction of acetylene according to *pathway a*.

4 Conclusions

In this study, it is demonstrated that Ag allows the exhaustive electrochemical dechlorination of highly toxic PyCEs to acetylene and ethylene under fairly mild conditions. Ag shows high catalytic activities for the reduction of PCE, TCE and 1,1-DCE, but not for 1,2-DCE, suggesting a deep influence of the chemical structure of the target molecules on the catalytic activity of the metal. The catalytic activity is further enhanced by the presence of proton donors such as H_2O or HAc, which probably accelerate the rate of regeneration of the active sites on the metal surface. In addition, the electrode remains active during long lasting electrolyses, which demonstrates its good resistance to surface fouling.

Electroreduction of PCE occurs by α,β -elimination of 2Cl^- to generate dichloroacetylene, which can be further reduced to acetylene in two consecutive steps with the consumption of 4e^- and 2H^+ . The electroreduction of TCE presents some more complications, since in this case the presence of an electrogenerated base in solution may trigger α,β -elimination of TCE involving the expulsion of H^+ and Cl^- to give dichloroacetylene, which can be further reduced to acetylene. The principal products of PCE and TCE reduction at Ag are acetylene and ethylene, the latter arising from reduction of the former. Therefore, Ag is a

promising electrode material not only for the abatement of dangerous PyCEs but also for the development of an electrochemical process for the conversion of PCE and TCE, formed as by-products in the synthesis of VCM process, to ethylene which can be recycled in the oxychlorination stage of the synthesis (Fig. 1, dashed pathway).

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